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(21) International Application Number: PCT/IB99/01196 (22) International Filing Date: 22 June 1999 (22.06.99) (30) Priority Data: 09/103,514 23 June 1998 (23.06.98) US (71) Applicant: FORD GLOBAL TECHNOLOGIES, INC. [US/US]; 600 Parklane Towers East, Dearborn, MI 48331 (US). (72) Inventors: RYTENZ, Rose, Ann; 36056 Farmbrook, Clinton Township, MI 48035 (US). BLAIS, Edmund, Joseph; 8780 Disputed Road, R.R.#3, Windsor, Ontario N9A 6Z6 (CA). HELMS, Jeffrey, Hampton; 368 Ann, Plymouth, MI 48170 (US).		(81) Designated States: CN, JP, European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report.</i>
(54) Title: CONDUCTIVE MODIFICATION OF PAINTABLE, MOULD-IN COLOUR CAPABLE, THERMOPLASTIC OLEFIN FORMULATIONS (57) Abstract A electrical conductivity modified thermoplastic olefin (TPO) polymer blend with improved electrostatic painting efficiency, the blend comprising a substantially uniform mixture of: I. Polymeric material being the reaction product of: (a) polypropylene, (b) maleated polypropylene, (c) elastomer, and (d) amine-terminated polyether being a linear or branched polymer of oxypropyleneamine or oxyethyleneamine repeating units having 40-100 such units, and II. alkali metal salt, the alkali metal salt being included in the thermoplastic polymer blend in an amount which provides the blend with a conductivity of at least 10^{-12} S/cm at 25 °C.		

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**CONDUCTIVE MODIFICATION OF PAINTABLE,
MOULD-IN COLOUR CAPABLE, THERMOPLASTIC OLEFIN FORMULATIONS**

The invention is directed to a modified thermoplastic
5 olefin blend (TPO) including an amine-terminated polyether
and maleated polypropylene whose electrical conductivity is
improved by adding thereto alkali metal ions.

Electrostatic painting of substrates is desirable
because it can reduce paint waste and solvent emissions as
10 compared to non-electrostatic painting techniques.
Electrostatic painting techniques, however, require the
substrate to be electrically conducting. If the material is
itself not electrically conducting, to provide increased
paint transfer efficiency during electrostatic painting, the
15 material is required to be made conducting. This can be
done by using an applied prepcoat which is electrically
conducting. In the past, injection moulded articles made
from electrically insulating thermoplastic materials like
XENOY™ or thermoplastic olefin (TPO), used such an applied
20 conducting primer to improve electrostatic painting.
Applying such prepcoats increases manufacturing complexity.

The invention of US patent 5,484,838 improves on such
surface conductivity imparting methods by disclosing a
thermoplastic polymer blend which had increased electrical
25 conductivity throughout the bulk of the substrate bulk
material. This bulk conductivity was provided by the
addition of electrically conductive carbon black to the
polymer blend. In particular, the blend comprises at least
a crystalline polymer and an amorphous or semi-crystalline
30 polymer wherein at least a portion of the carbon black is
dispersed within the crystalline polymer. Such electrically
modified bulk material, particularly TPO, is used in the
automotive industry in a variety of moulded articles
including bumper fascias, instrument panels, and mirror
35 housings painted by electrostatic methods. Since carbon is
black, it imparts a black colour to the final product. An
adhesion promoting layer is generally applied to this carbon

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black modified TPO before application of a basecoat and clearcoat in order to improve adhesion to the TPO.

The invention is a modified thermoplastic olefin (TPO) polymer blend with improved electrical conductivity, particularly useful to improve electrostatic painting efficiency of the plastic material. The modified TPO plastic blend comprises a substantially uniform mixture of polymeric material and alkali metal salts. The alkali metal salt is included in the polymer blend in an amount which provides said blend with a conductivity of at least 10^{-12} S/cm at 25°C.

The polymeric material is the reaction product of components: (a) polypropylene, (b) maleated polypropylene, (c) elastomer, and (d) amine-terminated polyether which is a linear or branched polymer of oxypropyleneamine or oxyethyleneamine repeating units having 10-100 such units. The polypropylene has a number average molecular weight of 30,000-120,000, 40-50% crystallinity, and melt flow rate of 1-10 dg/min.. The maleated polypropylene has a number average molecular weight of 10,000-60,000. The elastomer has a number average molecular weight of 23,000-50,500, 10-50% crystallinity, and melt flow rate of 1.2-9.0 dg/min.

In forming the blend, the alkali metal salt is preferably, but not necessarily, mixed with the amine-terminated polyether prior to its reaction with the other polymer components. The amine-terminated polyether can be reacted with maleated polypropylene prior to its reaction with the other polymer components.

The present invention has an advantage that it provides a plastic material useful in automotive applications which can be partially painted electrostatically while being coloured other than black. That is, to be able to be coloured to match or compliment the colour of an automotive vehicle. The plastic material may be painted without an applied primer coat to improve adhesion between of the paint and the TPO substrate.

According to another embodiment of the invention, it is the method of making the electrically conductive polymer blend disclosed above.

As disclosed above, the invention is a conductively modified thermoplastic olefin polymer (TPO) blend which has improved electrostatic painting efficiency. This modified blend is able to be manufactured, e.g., by extrusion, and formed into components which may be painted as desired. Advantageously, since the blend has been made conductive through the addition of alkali metal salts, it can be painted using commercially desirable electrostatic painting techniques. As disclosed above, electrostatic painting techniques allow more environmentally and commercially efficient painting of components. In addition, since the alkali metal salts are colourless, as compared to the black colour of carbon black, their addition to the TPO blend does not impart colour. Hence, not all of the component needs to be painted, rather use of the present invention material allows for the part to be moulded-in-colour and only part of the component to be painted. This is because it can be made various colours since alkali metals do not impart colour, not just black as when carbon is used. These colours can be such to match or compliment the item with which it is used. For example, if used in automotive vehicle applications like bumper fascias, it can be a colour associated with the vehicle, and does not need to be black. It is apparent that moulded-in-colour parts provide enhanced design opportunities in automotive applications.

Further the inventors have found, that conductive plastics of the present invention provide enhanced adhesion to paint thereto, obviating the need for primer coats generally provided on TPO to help adhere the decorative topcoats applied to the TPO plastic. The commercial manufacturing advantage in terms of cost and time is apparent.

As disclosed above, the modified plastic of the present invention comprises a substantially uniform mixture of a (I)

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polymeric material which forms the plastic aspect of the blend and (II) alkali metal salt which imparts electrical conductivity thereto. In particular, the polymeric material is the reaction product of these four components: (a) 5 polypropylene, (b) maleated polypropylene, (c) elastomer, and d) amine-terminated polyether (known in the art field as Jeffamine) which is a linear or branched polymer of oxypropyleneamine or oxyethyleneamine repeating units. Polyoxyethyleneamine has the chemical formula: $\text{NH}_2\text{CH}(\text{CH}_3)\text{CH}_2-$ 10 $(\text{OCH}_2\text{CH}_2)_n-\text{NH}_2$ and polyoxypropyleneamine has the chemical formula: $\text{NH}_2\text{CH}(\text{CH}_3)\text{CH}_2-(\text{OCH}_2\text{CH}(\text{CH}_3))_n-\text{NH}_2$. The amine-terminated polyether has 10-100, preferably 20-60 repeating units (i.e., $n = 10-100$).

In forming the blend, the four above discussed polymers 15 will be reacted. One reaction generally expected to take place during compounding is between a slight excess of the amine-terminated polyether and the maleated polypropylene, i.e., when the amine-terminated polyether is grafted to the polypropylene. That is, it is expected that the amine end- 20 group of one mole of the amine-terminated polyether reacts with the maleic anhydride functionality of 1.01 to 1.05 mole of the maleated polypropylene, however these proportions are not critical. As is known in the art, a maleated polypropylene and that useful in this invention has the 25 general chemical formula: $\text{CH}_3\text{CH}_2\text{CH}_2-(\text{CH}(\text{CH}_3)\text{CH}_2\text{C}_4\text{H}_3\text{O}_3)_n-$ with a number average molecular weight of 10,000 to 60,000. Generally, optimal maleated polypropylene for the present invention also have a viscosity of 35-250 cps at 160°C, a density of 0.88-0.93 g/cm³, and an acid number of 10-45.

30 Generally formation of the grafted amine-terminated polyether would take place during mixing of the components in an extruder, but alternatively can be done off-line if it is desired to first separately graft the amine-terminated polyether to the maleated polypropylene. If the latter is 35 carried out, i.e., off line, this grafted amine-terminated polyether would then be compounded with the last two

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components, the polypropylene and the elastomer, during processing as by extrusion.

Polypropylenes useful in the present invention have a number average (Mn) molecular weight of 30,000-120,000, more preferably being 50,000-80,000. Their crystallinity is 40-50% and melt flow rate is 1-70 dg/minute. Examples of polypropylenes useful in the present invention are Exxon Chemical Company Escorene 1042 with a density of 0.905 g/cm³, melt flow rate of 1.9 dg/min, Mn of approximately 67,070, Mw/Mn equal to 3.51, and flexural modulus equal to 1240 MPa and Escorene 1105 with a density of 0.906 g/cm³, melt flow rate equal to 34 dg/min, Mn of approximately 48,021, Mw/Mn equal to 2.58, and a flexural modulus of 1170 MPa. Still others will be apparent to those skilled in the art in view of the present disclosure.

The fourth polymeric component used to form the blend is an elastomer having crystallinity of 10-50%, melt flow rates of 1.2 to 9.0 dg/min, and number average molecular weights of 23,000 to 50,500. Such elastomers may include ethylene propene, ethylene butene, ethylene hexene or ethylene octene, to name but a few. Still others will be apparent to those skilled in the art in view of the teachings herein. Exemplary of such materials are Exxon Chemical Company Exact 4033, 3125, and/or 3022 (ethylene-butylene copolymers) with a Mw/Mn of 1.95 to 2.65.

Generally in forming the present invention polymer blend, the materials are utilised in the following amounts by weight: 55-75 parts polypropylene, 8-15 parts maleated polypropylene, 2-10 parts amine terminated polyether, and 10-25 parts elastomer. More preferred are blends with 60-70 parts polypropylene, 10-12 parts maleated polypropylene, 4-6 parts amine terminated polyether particularly with ethylene oxide repeat units, and 10-22 parts elastomer, particularly being ethylene-butylene copolymer elastomer.

In applications with stringent low temperature impact requirements, the elastomer level will typically represent 20-25 percent of the composition. Polypropylene content is

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largely dependent on the required modulus of the resulting blend with higher polypropylene content in stiffer materials.

The blend according to the present invention has an electrical conductivity of at least 10^{-12} S/cm at 25°C. In order to impart this electrical conductivity, alkali metal salts are incorporated in the blend. The alkali metal ions that can be used include, but are not limited to, lithium, sodium, and potassium. The salt may be of chlorides, e.g., lithium chloride, bromides, thiocyanides, hexafluorophosphates, acetates, trifluoromethane sulfonates, and mixtures of any of them. It is believed that the polyethylene oxide (EO) and polypropylene oxide (PO) units of the of the amine-terminated polyether acts to solvate the alkali metal salts therefore providing ionic conductivity to the injection moulded paintable TPO parts while maintaining substrate paintability. However, neither the understanding nor validity of this theory is necessary for practice of this invention.

The salt is added to the polymer blend or can be added first to the graft of the maleated polypropylene and amine-terminated polyether followed by the addition of this adduct with the remaining polymer components. The amount of salt added is defined in terms of the molar ratios of the ethylene oxide or propylene oxide repeat units to alkali metal cation. This ratio is desirably in the range of 5/1-30/1. For instance, for an ethylene oxide amine-terminated polyether, the number of ethylene oxide repeat units is approximately 24. Therefore 1 mole of the amine-terminated polyether represents 24 moles of the ethylene oxide repeat unit. To make a 10/1 ratio with alkali metal salt, 2.4 moles of alkali metal salt is required.

Prior to the present invention, it is believed by the present inventors that parts manufactured from TPO required the application of an adhesion promoting layer prior to application of the basecoat and clearcoat for good adhesion. And in the absence of an electrically conducting adhesion

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promoter and/or primer, the electrostatic painting efficiency for basecoat and clearcoat decreases by 50% because dissipation of electrical charge to ground cannot be efficiently accomplished. In order to maintain high

5 painting efficiencies and realisation of the cost savings associated with removal of the adhesion promoter and/or primer, conductive modification of the paintable TPO resin is necessary. Initial attempts to conductive modification of paintable TPO using the high structure conductive carbon
10 black approach has shown a significant interaction between the carbon black and the amine. This interaction both increases the necessary carbon level for acceptable electrostatic dissipation and decreases the adhesion of the basecoat to the substrate. Presumably, this interaction is
15 associated with the polarity of the amine and the high surface area of the conductive carbon black.

The alkali metal is included in the polymer blend in an amount which provides said blend with a conductivity of at least 10^{-12} S/cm at 25°C. In forming the blend, the alkali
20 metal salt is preferably be mixed with the amine-terminated polyether prior to its reaction with the other polymer components. As disclosed above, the amine-terminated polyether can also be reacted with maleated polypropylene prior to its reaction with the other polymer components.
25 Thus most preferably, it would be optimal to form the grafted amine-terminated polyether and then mix the alkali metal salt with the grafted amine-terminated polyether, which would then be mixed with the remaining components in the extruder where they would react to form the final
30 conductive blend.

As would be apparent to those skilled in the art of making plastic materials, other additives such as stabilisers are included in polymer blends during processing and for long term photochemical stability. For example,
35 such conventionally added materials may include, but are not limited to antioxidants such as sterically hindered phenols, phosphites, phosphonites, sterically hindered amine light

stabilisers, and ultraviolet light absorbers. And, as would be appreciated by those skilled in the art in view of the present disclosure, the addition of internal mould release agents such as metal stearates, fatty and wax acids, amides, or esterified polyol esters and lubricants such as thioesters, low molecular weight olefinic waxes, glycerol monostearate or ethoxylated fatty amines may be used as processing aides.

The table below lists the components of modified plastics made according to embodiments of the present invention as detailed in the examples. It also shows the results of paint adhesion tests on these materials.

Example #	1	2	3	4
	Components (Wt%)			
Polypropylene (PP)	64	60	60	75
Maleated PP	10	10	12	10
Jeffamine	4	6	5	4
Alkali Metal Salt				
LiCl		1.2		
LiCF ₃ SO ₃	2			1
KCl			1.5	
Ethylene-Butylene Rubber 20		22	21.04	10
Carbon Black			0.06	
TiO ₂			0.50	
Adhesion (% pass)	100	100	100	95
Conductivity (S/cm)	10 ⁻⁹	10 ⁻¹⁰	10 ⁻¹¹	10 ⁻⁹

Example 1

10 parts of Eastman T43 maleated polypropylene, 4 parts of Jeffamine (amine-terminated polyoxyethylene), and 2 parts lithium trifluoromethanesulfonate are blended in a single screw extruder with a barrel temperature of 190°C. and pelletised. To this reaction product is added 64 parts of polypropylene (Escorene 1042) and 21 parts of ethylene-butylene rubber (Exact 4033). The entire blend is compounded on a twin screw extruder with heater zones controlled at 200-220°C, extruded and pelletised. Samples

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are then injection moulded, painted with a one component basecoat and one or two component clearcoat and cured at 121°C for 30 minutes. Adhesion was checked via a cross-hatch adhesion test method 72 hours after the paint bake cycle.

- 5 Volume resistivity measurements were conducted according to ASTM D257-66 resulting in a value of 2.5×10^{-9} S/cm.

Example 2

1.2 parts of lithium chloride is combined with 6 parts
10 of Jeffamine and mixed above the Jeffamine melting point until dissolved. This mixture is then added to 10 parts of Eastman T43 maleated polypropylene and mixed on a single screw extruder at 190°C to complete the graft of the polyoxyethylene diamine to the polypropylene chain. This
15 melt product is then fed into a separate twin screw extruder along with 60 parts of polypropylene (Escorene 1105) and 22 parts of ethylene-butylene rubber (Exact 3035) and compounded at 210°C and pelletised. Samples were painted and tested as in Example 1.

20

Example 3

60 parts of polypropylene (Escorene 1042), 12 parts of Eastman T43 maleated polypropylene, 5 parts of Jeffamine, 1.5 parts of potassium chloride, 21.04 parts of ethylene-
25 butylene rubber (Exact 3022), 0.06 parts of carbon black, and 0.5 parts of titanium oxide were added to a Banbury mixer and blended at 200 rpm for 4 minutes. The resulting blend was passed through a single screw extruder operated at 190°C and pelletised. Parts were injection moulded and
30 painted as in Example 1. The resulting paint adhesion was good and the volume resistivity was measured to be 1×10^{-11} S/cm. This material is a mould-in-colour grey plastic which is suitable for partially painted applications.

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Example 4

10 parts of Eastman T43 maleated polypropylene was blended with 4 parts of Jeffamine and 1 part of lithium

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trifluoromethane sulphonate on a single screw extruder operated at 190°C and pelletised. These pellets were then blended with 75 parts of polypropylene (Escorene 1105) and 10 parts of ethylene-butylene rubber (Exact 3022) on a twin
5 screw extruder operated at 200°C and repelletised prior to injection moulding. Injection moulded plaques tested for volume resistivity and then painted and tested cross-hatch adhesion. 95 percent adhesion was achieved with a volume resistivity of 1×10^{-9} S/cm.

10

These examples may be repeated with similar success by substituting the generically or specifically described reactants and/or reactant conditions recited herein for those actually used in the preceding example.

CLAIMS

1. A thermoplastic olefin polymer blend which has been
conductively modified to improve electrostatic painting
5 efficiency, the modified blend comprising a uniform mixture
of:

I. polymeric material being the reaction product of:

(a) polypropylene having a number average molecular
weight of 30,000-120,000, 40-50% crystallinity, and melt
10 flow rate of 1-10 dg/min.;

(b) maleated polypropylene having a number average
molecular weight of 10,000-60,000;

(c) elastomer having a number average molecular weight
of 23,000-50,500, 10-50% crystallinity, and melt flow
15 rates of 1.2-9.0 dg/min;

(d) amine-terminated polyether being a linear or
branched polymer of oxypropyleneamine or oxyethyleneamine
repeating units having 10-100 such units, and

II. alkali metal salt, the alkali metal salt being
20 included in said polymer blend in an amount which provides
said blend with a conductivity of at least 10^{-12} S/cm at 25°C.

2. A modified thermoplastic polymer blend according
to claim 1, wherein said alkali metal salt is mixed with
25 said amine-terminated polyether prior to reaction thereof
with said other polymer blend materials.

3. A modified thermoplastic polymer blend according
to claim 1 or 2, wherein said amine-terminated polyether is
30 reacted with said maleated polypropylene (I) prior to
reaction with said other polymer blend materials.

4. A modified thermoplastic polymer blend according
to any one of claims 1 to 3, wherein said alkali metal salts
35 are selected from lithium, sodium, and potassium salts.

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5. A modified thermoplastic polymer blend according to any one of the preceding claims, wherein said salts are selected from chlorides, bromides, thiocyanides, hexafluorophosphates, acetates, and trifluormethane sulfonates.

6. A modified thermoplastic polymer blend according to any one of the preceding claims, wherein said blend comprises, by weight, 55-75 parts polypropylene, 8-15 parts maleated polypropylene, 2-10 parts amine terminated polyether, and 10-25 parts elastomer.

7. A moulded thermoplastic article, having a modified electrical conductivity, adapted for electrostatic painting, being comprised of the modified thermoplastic polymer blend of any one of the preceding claims.

INTERNATIONAL SEARCH REPORT

International Application No.

PCT/IB 99/01196

A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C08L23/12 C08L51/06 • //(C08L23/12,51:06,23:08,C08K3:00)

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C08L C08K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	WO 97 03108 A (HUNTSMAN SPEC CHEM CORP) 30 January 1997 (1997-01-30) page 2, line 15 - page 4, line 7 page 13, line 5 - line 10 page 14, line 1 - page 15, line 5; example 1; table 1A	1-7
Y	EP 0 421 612 A (DAI ICHI KOGYO SEIYAKU CO LTD) 10 April 1991 (1991-04-10) page 2, line 4 - page 3, line 29	1-7

☐

Further documents are listed in the continuation of box C.

☒

Patent family members are listed in annex.

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INTERNATIONAL SEARCH REPORT

Information on patent family members

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